CAAP Quarterly Report

Date of Report: *March. 31st, 2017*

Contract Number: *DTPH56-16-H-CAAP03*

Prepared for: *U.S. DOT Pipeline and Hazardous Materials Safety Administration*

Project Title: Development of New Multifunctional Composite Coatings for Preventing and Mitigating Internal Pipeline Corrosion

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For quarterly period ending: *March. 31st, 2017*

Business and Activity Section

(a) Generated Commitments

No changes to the existing agreement

Purchase including nano-materials has been made over this reporting period

(b) Status Update of Past Quarter Activities

The research activities in the second quarter consist of material screening, test methods identification and baseline tests in Task 2, as summarized below.

Task 2: Synthesize, characterize and optimize the new coatings

The research group in this stage is focusing on three most relevant properties of the new coatings, including anti-corrosion, anti-fouling, and abrasion resistance. A specific plan of experimental study was discussed during the weekly meeting after last quarterly report submission. All these three properties will be classified for the new coating as compared to the baseline coatings (existing commercial coatings). Consider a large number of variables for designing the new nanomaterial-based composite, screening materials and test methods are carefully selected, which could potentially allow high efficiency.

Summary of work for Task 2.1 and 2.2. in polymer binders and the nano-modified additives.

The summarized works [1-31] show the possibility using nanomaterials to fabricate high-performance coatings and the potential approaches into polymer matrix.

The literature study has been done on the developed test methods for determining the quality of the coatings, including corrosion resistance test, abrasion resistance test and antifouling test.

(a) Abrasion test methods

The accelerated test (ASTM G6) is used for determining the relative abrasion resistance of steel pipe coating. The test apparatus (from RAE Coatings Lab) for this test in the revolving drum. The drum, which containing nine coated pipe sample, will fill with a slurry of coarse abrasive and water during the test.

Once the drum starts to rotate by the motor, the wet coarse abrasive will impact the coated surface will damage the coating. Even this test is specifically designed for the pipe coating. The coated surfaces are the exterior surface of the pipelines instead on the internal surface of the pipe.

The mechanism of falling abrasive (ASTM D968) and Taber Abraser (ASTM D4060) methods are very similar as they both apply abrasion on a coated panel. Both test methods require the coating is applied at a uniform thickness on a rigid panel.

(b) Fouling resistance test methods

There are several well-developed experimental apparatuses have been designed to study fouling in the lab. Even the fouling mechanism for the crude oil is much different and complicated compared with the fouling in transmission pipes; the test method might be modified in the future if necessary. Two test methods are discussed in this report: are hot wire method, closed liquid system microbomb.

(c) Lab study for characterizing baseline coatings and nanomaterial-based composites

For the proposed new multifunctional composite coatings, like discussed earlier, the three main objectives are anti-corrosion, anti-fouling, and abrasion resistance. All these three properties must be tested for both baseline coating (existing commercial coatings) and developed nanomaterial-based composites. In this chapter, the methodology of characterizing baseline coating and nanomaterial-based composites will be discussed. The coated samples has been prepared om Q-panel standard steel panels. Falling Abrasive method has been used to the abrasion resistance as shown in Fig. 1. For corrosion resistance, Potentiostatic EIS test has been performed to evaluate the protective coatings. Hydrophobicity can be used to determine the fouling resistance indirectly as the droplet contact angle shows the ability of a liquid to maintain contact with the coated surface.

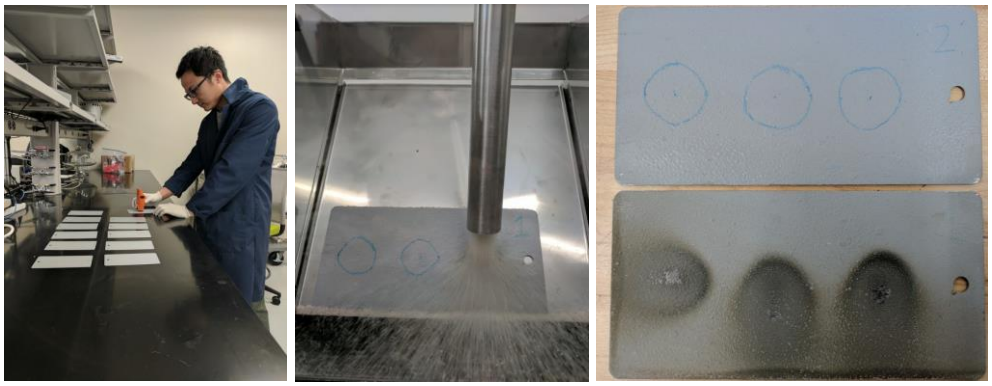

Figure 1 Falling abrasive test

To characterize the barrier properties of the coatings, EIS test was perfumed for coated samples as well. The sample was immerged in the 3.5% NaCl solution. Both samples have the identical setup and the EIS data was shown in Figure 4, where the impedance modulus |Z| is plotted as a function of the frequency in EIS tests.

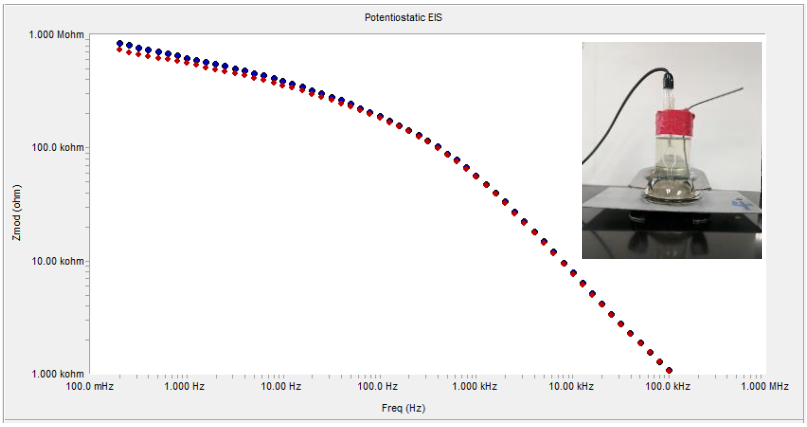

Figure 2 EIS results for a baseline coating

(c) Description of any Problems/Challenges

No problems are experienced during this report period

(d) Planned Activities for the Next Quarter

The planned activities for next quarter are listed below:

- Synthesize and characterize synthesize the nano-modified coatings
- Characterize and optimize the new coatings

References

[1] V. N. Mochalin and Y. Gogotsi, "Nanodiamond–polymer composites," *Diam. Relat. Mater.*, vol. 58, pp. 161–171, 2015.

[2] X.-L. Xie, Y.-W. Mai, and X.-P. Zhou, "Dispersion and alignment of carbon nanotubes in polymer matrix: a review," *Mater. Sci. Eng. R Rep.*, vol. 49, no. 4, pp. 89–112, 2005.

[3] S. Shadlou, E. Alishahi, and M. Ayatollahi, "Fracture behavior of epoxy nanocomposites reinforced with different carbon nano-reinforcements," *Compos. Struct.*, vol. 95, pp. 577–581, 2013.

[4] J. N. Coleman, U. Khan, W. J. Blau, and Y. K. Gun'ko, "Small but strong: a review of the mechanical properties of carbon nanotube–polymer composites," *Carbon*, vol. 44, no. 9, pp. 1624–1652, 2006.

[5] S. Roy, K. Mitra, C. Desai, R. Petrova, and S. Mitra, "Detonation nanodiamonds and carbon nanotubes as reinforcements in epoxy composites—a comparative study," *J. Nanotechnol. Eng. Med.*, vol. 4, no. 1, p. 11008, 2013.

[6] V. Singh, D. Joung, L. Zhai, S. Das, S. I. Khondaker, and S. Seal, "Graphene based materials: past, present and future," *Prog. Mater. Sci.*, vol. 56, no. 8, pp. 1178–1271, 2011.

[7] V. Georgakilas, J. A. Perman, J. Tucek, and R. Zboril, "Broad family of carbon nanoallotropes: classification, chemistry, and applications of fullerenes, carbon dots, nanotubes, graphene, nanodiamonds, and combined superstructures," *Chem. Rev.*, vol. 115, no. 11, pp. 4744–4822, 2015.

[8] J. Slonczewski and P. Weiss, "Band structure of graphite," *Phys. Rev.*, vol. 109, no. 2, p. 272, 1958.

[9] K. S. Novoselov *et al.*, "Electric field effect in atomically thin carbon films," *science*, vol. 306, no. 5696, pp. 666–669, 2004.

[10] A. A. Balandin *et al.*, "Superior thermal conductivity of single-layer graphene," *Nano Lett.*, vol. 8, no. 3, pp. 902–907, 2008.

[11] C. Lee, X. Wei, J. W. Kysar, and J. Hone, "Measurement of the elastic properties and intrinsic strength of monolayer graphene," *science*, vol. 321, no. 5887, pp. 385–388, 2008.

[12] M. S. Dresselhaus, A. Jorio, M. Hofmann, G. Dresselhaus, and R. Saito, "Perspectives on carbon nanotubes and graphene Raman spectroscopy," *Nano Lett.*, vol. 10, no. 3, pp. 751–758, 2010.

[13] S. G. Miller *et al.*, "Characterization of epoxy functionalized graphite nanoparticles and the physical properties of epoxy matrix nanocomposites," *Compos. Sci. Technol.*, vol. 70, no. 7, pp. 1120–1125, 2010.

[14] M. Ayatollahi, E. Alishahi, S. Doagou-R, and S. Shadlou, "Tribological and mechanical properties of low content nanodiamond/epoxy nanocomposites," *Compos. Part B Eng.*, vol. 43, no. 8, pp. 3425–3430, 2012.

[15] A. T. Dideikin, "Applications of Detonation Nanodiamonds," *Detonation Nanodiamonds Sci. Appl.*, p. 239, 2014.

[16] J.-L. Tsai and T.-C. Lu, "Investigating the load transfer efficiency in carbon nanotubes reinforced nanocomposites," *Compos. Struct.*, vol. 90, no. 2, pp. 172–179, 2009.

[17] G. Zhang, J. Karger-Kocsis, and J. Zou, “Synergetic effect of carbon nanofibers and short carbon fibers on the mechanical and fracture properties of epoxy resin,” *Carbon*, vol. 48, no. 15, pp. 4289–4300, 2010.
[18] J. R. Potts, D. R. Dreyer, C. W. Bielawski, and R. S. Ruoff, “Graphene-based polymer nanocomposites,” *Polymer*, vol. 52, no. 1, pp. 5–25, 2011.
[19] X. Wang, H. Yang, L. Song, Y. Hu, W. Xing, and H. Lu, “Morphology, mechanical and thermal properties of graphene-reinforced poly (butylene succinate) nanocomposites,” *Compos. Sci. Technol.*, vol. 72, no. 1, pp. 1–6, 2011.
[20] T. Kuilla, S. Bhadra, D. Yao, N. H. Kim, S. Bose, and J. H. Lee, “Recent advances in graphene based polymer composites,” *Prog. Polym. Sci.*, vol. 35, no. 11, pp. 1350–1375, 2010.
[21] W. Zheng, X. Lu, and S.-C. Wong, “Electrical and mechanical properties of expanded graphite-reinforced high-density polyethylene,” *J. Appl. Polym. Sci.*, vol. 91, no. 5, pp. 2781–2788, 2004.
[22] M. A. Aldosari, A. A. Othman, and E. H. Alsharaeh, “Synthesis and characterization of the in situ bulk polymerization of PMMA containing graphene sheets using microwave irradiation,” *Molecules*, vol. 18, no. 3, pp. 3152–3167, 2013.
[23] K. Kalaitzidou, H. Fukushima, and L. T. Drzal, “A new compounding method for exfoliated graphite–polypropylene nanocomposites with enhanced flexural properties and lower percolation threshold,” *Compos. Sci. Technol.*, vol. 67, no. 10, pp. 2045–2051, 2007.
[24] B. Pan, J. Zhao, Y. Zhang, and Y. Zhang, “Wear performance and mechanisms of polyphenylene sulfide/polytetrafluoroethylene wax composite coatings reinforced by graphene,” *J. Macromol. Sci. Part B*, vol. 51, no. 6, pp. 1218–1227, 2012.
[25] I. Neitzel, V. Mochalin, I. Knoke, G. R. Palmese, and Y. Gogotsi, “Mechanical properties of epoxy composites with high contents of nanodiamond,” *Compos. Sci. Technol.*, vol. 71, no. 5, pp. 710–716, 2011.
[26] J. Liang *et al.*, “Molecular-level dispersion of graphene into poly (vinyl alcohol) and effective reinforcement of their nanocomposites,” *Adv. Funct. Mater.*, vol. 19, no. 14, pp. 2297–2302, 2009.
[27] K. Bin Rostani, “Effect of Crude Oil Vanadyl Porphyrin Content and Blending on Heat Exchanger Fouling,” 2013.
[28] J. Escobedo and G. Ali Mansoori, “Heavy-organic particle deposition from petroleum fluid flow in oil wells and pipelines,” *Pet. Sci.*, vol. 7, no. 4, pp. 502–508, 2010.
[29] T. Stephenson *et al.*, “Corrosion-fouling of 316 stainless steel and pure iron by hot oil,” *Energy Fuels*, vol. 25, no. 10, pp. 4540–4551, 2011.
[30] Q. Zhou, “Flow accelerated organic coating degradation,” 2014.
[31] D. Loveday, P. Peterson, and B. Rodgers, “Evaluation of organic coatings with electrochemical impedance spectroscopy,” *JCT Coat. Tech*, vol. 8, pp. 46–52, 2004.